



US007233378B2

(12) **United States Patent**
Obayashi et al.

(10) **Patent No.:** **US 7,233,378 B2**
(45) **Date of Patent:** **Jun. 19, 2007**

(54) **ANTI-REFLECTION FILM, METHOD FOR PRODUCING THE SAME, AND IMAGE DISPLAY DEVICE**

(75) Inventors: **Tatsuhiko Obayashi**, Minami-ashigara (JP); **Takafumi Hosokawa**, Minami-ashigara (JP); **Kenichi Nakamura**, Minami-ashigara (JP); **Atsuhiko Okawa**, Minami-ashigara (JP)

(73) Assignee: **Fujifilm Corporation**, Minato-Ku, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 147 days.

(21) Appl. No.: **10/354,961**
(22) Filed: **Jan. 31, 2003**

(65) **Prior Publication Data**
US 2003/0175502 A1 Sep. 18, 2003

(30) **Foreign Application Priority Data**
Feb. 1, 2002 (JP) 2002-026092

(51) **Int. Cl.**
G02B 1/11 (2006.01)
(52) **U.S. Cl.** 349/137; 428/212; 428/323
(58) **Field of Classification Search** 349/137; 428/323

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,210,858 B1 *	4/2001	Yasuda et al.	430/270.1
6,217,176 B1 *	4/2001	Mackawa	359/601
6,383,559 B1	5/2002	Nakamura et al.	
6,686,031 B2 *	2/2004	Matsufuji et al.	428/212
6,710,923 B2 *	3/2004	Ito	359/599
6,731,363 B2 *	5/2004	Nakamura et al.	349/137
6,791,649 B1 *	9/2004	Nakamura et al.	349/137

FOREIGN PATENT DOCUMENTS

JP	2001-166104 A	6/2001
JP	2001-188104	7/2001

* cited by examiner

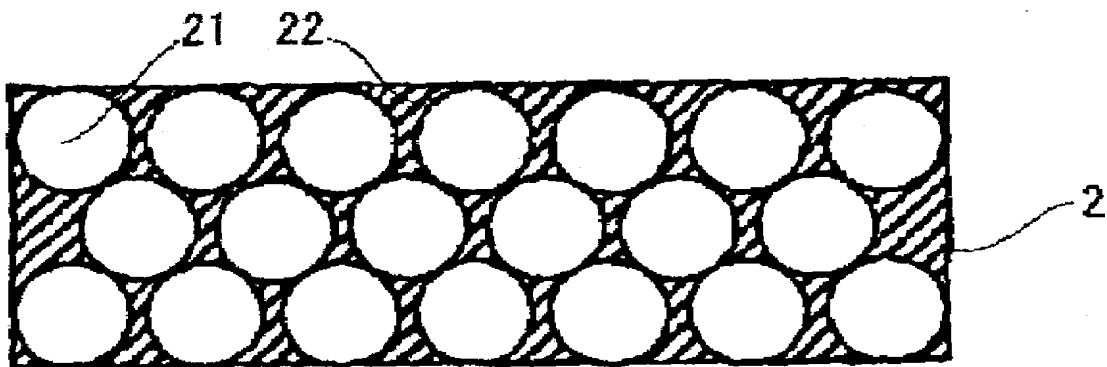
Primary Examiner—H. Thi Le

(74) *Attorney, Agent, or Firm*—Buchanan Ingersoll & Rooney PC

(57) **ABSTRACT**

An anti-reflection film containing a high-refractive-index layer having a refractive index of 1.65 to 2.40 and a low-refractive-index layer having a refractive index of 1.20 to 1.55, wherein the high-refractive-index layer is formed by coating and hardening a coating solution composition that contains inorganic fine particles having an average particle size of 1 to 200 nm and being dispersed with a polymer having a crosslinkable group. A method of producing the anti-reflection film and an image display device provided with the anti-reflection film.

22 Claims, 1 Drawing Sheet



particles, manufactured by Ishihara Sangyo Kaisha, Ltd.), 4.5 mass parts of a crosslinkable group-containing polymer P-(1), 0.3 mass part of a conventional cationic monomer (DMAEA (Trade name), N,N-dimethylamino ethylacrylate, manufactured by Kohjin Co., Ltd.), and 65.2 mass parts of cyclohexanone were dispersed by means of a sand grinder mill, to prepare a dispersion of titanium dioxide having a mass-average particle size of 53 nm.

(Preparation of Coating Solution for Middle-Refractive-Index Layer)

To 49.06 g of the above-mentioned titanium dioxide dispersion, 18.08 g of dipentaerythritol hexaacrylate (DPHA (Trade name), manufactured by Nippon Kayaku Co., Ltd.), 0.920 g of a photopolymerization initiator (Irgacure 907 (Trade name), manufactured by Ciba-Geigy), 0.307 g of a photosensitizer (Kayacure DETX (Trade name), manufactured by Nippon Kayaku Co., Ltd.), 230.0 g of methylethylketone and 500 g of cyclohexanone were added and stirred. The mixture was filtered through a polypropylene filter having a mesh of 0.4 μ m, to prepare a coating solution of a middle-refractive-index layer.

(Preparation of Coating Solution for High-Refractive-Index Layer)

To 110.0 g of the above-mentioned titanium dioxide dispersion, 6.29 g of dipentaerythritol hexaacrylate (DPHA (Trade name), manufactured by Nippon Kayaku Co., Ltd.), 0.520 g of a photopolymerization initiator (Irgacure 907 (Trade name), manufactured by Ciba-Geigy), 0.173 g of a photosensitizer (Kayacure DETX (Trade name), manufactured by Nippon Kayaku Co., Ltd.), 230.0 g of methylethylketone and 460.0 g of cyclohexanone were added and stirred. The mixture was filtered through a polypropylene filter having a mesh of 0.4 μ m, to prepare a coating solution of a high-refractive-index layer.

(Preparation of a Coating Solution for a Low-Refractive-Index Layer)

8.0 g of a dispersion of silica particles in methylethylketone (MEK-ST (trade name), solid content concentration: 30% by mass, manufactured by Nissan Chemical Industries, Co., Ltd.) and 100 g of methyl isobutyl ketone were added to 93.0 g of a thermally crosslinkable fluorine-containing polymer (JN-7228 (trade name), a refractive index: 1.42, solid content concentration: 6% by mass, manufactured by JSR Corporation). The mixture was stirred, and then subjected to filtration using a polypropylene filter having a pore diameter of 1 μ m, to prepare a coating solution for a low-refractive-index layer.

(Preparation of a Coating Solution for a Hard Coat Layer)

125 g of a mixture of pentaerythritol pentaacrylate and dipentaerythritol hexaacrylate (DPHA (trade name), manufactured by Nippon Kayaku Co., Ltd.) and 125 g of urethane acrylate oligomer (UV-6300B (trade name), manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.) were dissolved in 439 g of an industrial modified ethanol. To the resultant solution was added a solution in which 7.5 g of a photopolymerization initiator (Irgacure 907 (trade name), manufactured by Chiba Geigy Co.) and 5.0 g of a photosensitizer (Kayacure DETX (trade name), manufactured by Nippon Kayaku Co., Ltd.) were dissolved in 49 g of methyl ethyl ketone. After the resultant mixture was stirred, the coating solution for a hard coat layer was prepared by filtration using a polypropylene filter having a 1 μ m mesh.

(Preparation of Anti-Reflection Film)

The above-mentioned coating solution of a hard coat layer was coated on a triacetyl cellulose film (TAC-DU (Trade name), manufactured by Fuji Photo Film Co., Ltd.) having a thickness of 80 μ m, by using a bar coater, and dried at 90° C. Thereafter, an ultraviolet ray was irradiated to the coating layer to harden the layer. Thus, a hard coat layer having a thickness of 6 μ m was formed.

The above-mentioned coating solution for a middle-refractive-index layer was coated on the hard coat layer by using a bar coater, and dried at 60° C. Thereafter, an ultraviolet ray was irradiated to the coating layer to harden the layer. Thus, a middle-refractive-index layer (refractive index: 1.70, coating thickness: 70 nm, TTB-55B: 21 volume %) was formed. The above-mentioned coating solution for a high-refractive-index layer was coated on the middle-refractive-index layer by using a bar coater, and dried at 60° C. Thereafter, an ultraviolet ray was irradiated to the coating layer to harden the layer. Thus, a high-refractive-index layer (refractive index: 1.95, coating thickness: 75 nm, TTB-55B: 51 volume %) was formed. The above-mentioned coating solution for a low-refractive-index layer was coated on the high-refractive-index layer by using a bar coater, and dried at 120° C. for 10 minutes. Thereafter, the temperature was allowed to cool down to room temperature, and the low-refractive-index layer (refractive index: 1.40, coating thickness: 85 nm) was formed. Thus, the anti-reflection film was prepared.

(Evaluation of Anti-Reflection Film)

The obtained anti-reflection film was evaluated on the following items:

(1) Evaluation of Average Reflectance

Spectral reflectance values were obtained at an incidence angle of 5 degrees in the wavelength region of 380 nm to 780 nm, by means of a spectrophotometer (manufactured by JASCO Corporation). Then, the average reflectance in the wavelength region of 450 to 650 nm was obtained.

(2) Evaluation of Haze

A haze value of the film was measured using a haze meter Model NHD-10001DP (trade name, manufactured by Nihon Denshoku Kogyo KK).

(3) Evaluation of Pencil Hardness Test

The anti-reflection film was humidified under the conditions of 25° C. and 60% R.H. for 2 hours. Thereafter, according to the evaluation method of the pencil hardness specified by JIS K5400, the pencil hardness at 1-kg load was evaluated using the testing pencil specified by JIS S6006.

(4) Evaluation of Scratch Resistance to Steel Wool

#0000 steel wool under a loading condition of 200 g/cm² was reciprocated 10 times. A state of scratch thereafter was observed, and evaluated according to the following five grades:

- A: No scratch observed.
- B: Scratches slightly observed, but hardly noticeable.
- C: Few scratches observed, and apparently noticeable.
- D: Remarkable scratches observed, but a few scratch-free portions.
- E: Scratches observed all over the surface.

(5) Evaluation of Saponification-Processing Resistance

A 1.5N aqueous solution of sodium hydroxide was prepared and kept at 50° C. The previously prepared anti-reflection film was soaked in the above-mentioned sodium hydroxide aqueous solution for 2 minutes, and then it was soaked in water to thoroughly wash away the sodium

27

hydroxide aqueous solution. Subsequently, the film was soaked in a 0.01N aqueous solution of dilute sulfuric acid for 1 minute, and then it was soaked in water to thoroughly wash away the dilute sulfuric acid aqueous solution. Thereafter, the anti-reflection film was sufficiently dried at 100° C. With the thus-obtained anti-reflection film, property evaluations shown in the above (1) to (4) were conducted.

The obtained results are shown in Table 1.

Example 2

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable polymer used for dispersing titanium dioxide was replaced with P-(7). The obtained results are shown in Table 1.

Example 3

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable polymer used for dispersing titanium dioxide was replaced with P-(11). The obtained results are shown in Table 1.

Example 4

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable polymer used for dispersing titanium dioxide was replaced with P-(14). The obtained results are shown in Table 1.

Example 5

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable polymer used for dispersing titanium dioxide was replaced with P-(16). The obtained results are shown in Table 1.

Example 6

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable polymer used for dispersing titanium dioxide was replaced with P-(17). The obtained results are shown in Table 1.

Example 7

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable

28

polymer used for dispersing titanium dioxide was replaced with P-(22). The obtained results are shown in Table 1.

Example 8

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable polymer used for dispersing titanium dioxide was replaced with P-(25). The obtained results are shown in Table 1.

Example 9

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable polymer used for dispersing titanium dioxide was replaced with P-(34). The obtained results are shown in Table 1.

Example 10

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable polymer used for dispersing titanium dioxide was replaced with P-(36) and the photopolymerization initiator in the coating solutions for the middle- and low-refractive-index layers was replaced with UV1699 (trade name, manufactured by UNION CARBIDE JAPAN KK), respectively. The obtained results are shown in Table 1.

Example 11

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that no cationic monomer (DMAEA (Trade name), manufactured by Kohjin Co., Ltd.) was added to the dispersion of titanium dioxide. The obtained results are shown in Table 1.

Comparative Example 1

(Formulation Described in JP-A-2001-166104)

An anti-reflection film was prepared and evaluated in the same manner as in Example 1, except that the crosslinkable polymer P-(1) used for dispersing titanium dioxide was replaced with a commercially available anionic monomer PM-21 (trade name, manufactured by Nippon Kayaku Co., Ltd.). The obtained results are shown in Table 1.

TABLE 1

	Before Saponification				After Saponification			
	Average Reflectance	Haze	Pencil Hardness	Steel Resistance	Average Reflectance	Haze	Pencil Hardness	Steel Resistance
Example 1	0.32%	0.2%	3H	A	0.32%	0.2%	3H	A
Example 2	0.33%	0.2%	3H	A	0.33%	0.2%	3H	A
Example 3	0.32%	0.2%	3H	A	0.32%	0.2%	3H	A
Example 4	0.33%	0.4%	3H	B	0.33%	0.4%	3H	C
Example 5	0.32%	0.3%	2H	C	0.32%	0.3%	2H	D
Example 6	0.32%	0.3%	3H	B	0.32%	0.3%	3H	B
Example 7	0.33%	0.2%	3H	B	0.33%	0.2%	3H	B
Example 8	0.32%	0.2%	3H	A	0.32%	0.2%	3H	A
Example 9	0.33%	0.4%	3H	B	0.33%	0.4%	3H	B
Example 10	0.33%	0.4%	3H	A	0.33%	0.3%	3H	B
Example 11	0.32%	0.3%	3H	B	0.32%	0.3%	3H	D
Comparative example 1	0.32%	0.3%	2H	C	0.32%	0.3%	<H	E

